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(54)

**Two-component dental impression materials.**

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Two-component dental impression materials based upon polyvinylsiloxane elastomers include a catalyst paste which comprises up to 20,000 ppm of finely-divided platinum black, which functions to adsorb hydrogen gas generated on reaction of the catalyst paste when mixed with a base paste containing hydrofunctional polydimethylsiloxane. The said paste desirably further contains a hydrophilic surfactant.

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1        TWO-COMPONENT DENTAL IMPRESSION MATERIALS

          The present invention relates to dental  
impression materials of the kind comprising two components  
which are mixed together in use and is concerned more  
5 particularly with two-component dental impression  
materials which comprise polyvinylsiloxane elastomers, the  
setting and hardening of which is catalysed by means of  
platinum black.

          The liberation of small quantities of hydrogen  
10 gas from RTV addition-cured polyvinylsiloxane elastomers,  
due to reaction between the platinum catalyst and  
hydrofunctional polydimethylsiloxane, is a recognised  
problem. The evolution of hydrogen gas results in the  
formation of pores in the model formed from the  
15 impression, producing an undesirable pitted surface.

          This problem is described in US-A-4,273,902  
and a solution to it is disclosed, based upon the  
use of 0.5 ppm or more of finely-divided palladium  
and/or a finely-divided palladium alloy containing  
20 10% by weight or more of palladium, without inhibiting  
the addition reaction. Various other elemental metals  
are cited in this publication, including platinum,  
but it is stated that these are inferior to palladium  
and fail to eliminate the undesirable pores in

1 the surface of the resulting model.

The adsorption of hydrogen by palladium is variously quoted as 502, 935 and even 2952 times its own volume, (see J. W. Mellor, Inorganic Chemistry, Vol XVII, 5 1947, page 616 et seq.,) while the adsorption of hydrogen by platinum black is quoted as 310 volumes in Vol XVI. It therefore becomes apparent that these adsorption variabilities arise from differences in the available surface areas of the finely-divided metals, but are not 10 significant in the case of the polyvinylsiloxane elastomer application since, if sufficiently finely-divided and present in adequate concentration, the adsorption saturation level will never be reached.

Another problem associated with 15 polyvinylsiloxane dental impression materials is their extremely hydrophobic characteristics, which lead to comparatively large bubble-shaped artifacts in the surface of such impressions.

Accordingly, it has been discovered that when 20 samples of extremely finely-divided platinum black are obtained with the highest possible surface area, specifically  $24 \text{ M}^2/\text{gram}$ , and are compared with equal weight percent concentrations of palladium black, by incorporation in identical polyvinylsiloxane elastomer 25 pastes, they are equally and completely effective, down to a concentration level of about 0.2 ppm by weight. An effective concentration range for the platinum black is from 0.2 to 20,000 ppm by weight. The size range for the platinum black should be as small as possible. A 30 preferred size range for the platinum black is from 18 to 28 Ångstrom Units.

The use of platinum black in accordance with the present invention allows the control or prevention of outgassing in all addition-cured polyvinylsiloxane 35 elastomers, which are primarily used in making dental impressions.

The platinum black is used to adsorb gaseous hydrogen generated during the curing reaction and

1 and generally is present at a concentration level in  
the range from 0.2 to 20,000 ppm. A preferred  
concentration range is from 0.001 to 0.01 weight  
percent (i.e., 1,000 to 10,000 ppm). The platinum  
5 black is added or blended with the catalyst paste in  
any convenient manner, such as described in  
US-A-4,273,902.

It has also been discovered, in accordance  
with a preferred embodiment of the invention, that the  
10 extremely hydrophobic characteristics of  
polyvinylsiloxane dental impression materials, which  
lead to comparatively large bubble-shaped artifacts in  
the surface of impressions made with them, can be  
overcome by the incorporation of relatively small  
15 quantities of selected surfactants.

In two-component dental impression materials  
according to this invention, both of the base and  
catalyst pastes contain vinyl polydimethylsiloxane and  
silica or other similar inert filler(s) and the base  
20 paste contains a moiety of hydrofunctional  
polydimethylsiloxane, whereas the catalyst contains  
both a chloroplatinic acid catalyst complex and  
platinum black, to adsorb any gaseous hydrogen formed  
during mixing of the pastes and curing of the  
25 impression.

A cured impression is produced by mixing the  
base paste and the catalyst, such as that illustrated  
in Example I below, in a 1:1 or other suitable ratio to  
form a homogeneous plastic mass, which is applied over  
30 the dentition and adjacent gingival tissue and allowed  
to cure during a time frame of several minutes prior to  
mouth removal. Models made from impressions taken with  
the platinum black-containing materials of the  
invention, immediately after mouth removal, are found  
35 to be free from pores in all cases, at or above the  
0.005 weight percent platinum level.

Impressions and resulting moulds or models  
formed using the compositions of the present invention

1 result in a surface smoothness which is significantly  
better than upon those formed without the use of  
platinum black.

Another problem associated with  
5 polyvinylsiloxane dental impression materials is caused  
by their extremely hydrophobic characteristics, which  
can lead to the formation of comparatively large  
bubble-shaped artifacts in the surface of such  
impressions.

10 US-A-4,600,751 discloses the controlled  
release of bioactive agents and serves to demonstrate  
the synthesis of silicone-based prepolymers which are  
extremely hydrophilic.

In dentistry, impression materials,  
15 particularly for making crown and bridge impressions,  
require a high degree of dimensional stability, to  
facilitate the production of extremely accurate  
prostheses, for which the techniques of US-A-4,600,751  
are totally unsuitable, because high water sorption is  
20 consistent with swelling and distortion of these  
polymers. Furthermore, there are other definite  
advantages to dental impressions with low water  
sorption, such as ease of disinfection and  
sterilization.

25 With respect to the problem associated with  
these hydrophobic characteristics, in the dental  
impression materials of the present invention, it has  
been found possible to utilize several species of  
hydrophilic compounds as low-concentration additives to  
30 conventional extremely hydrophobic addition-cured  
polyvinylsiloxane dental impression materials, so as to  
impart truly hydrophilic surface characteristics to  
these materials. This prevents the formation of  
comparatively large bubble-shaped artifacts in the  
35 surface of these impressions, due to the effects of  
surface tension at a strongly hydrophobic/hydrophilic  
interface causing a film of moisture to form water  
droplets.

1 In a preferred embodiment of this invention,  
 any one or more of the following surfactant type  
 compounds are added to conventional addition-cured  
 polyvinylsiloxane dental impression materials in  
 5 relatively low concentrations of about 1.0% to 10.0% by  
 weight.

	<u>COMPOUND NAME</u>	<u>CAS NO. WHERE KNOWN</u>
	n-dodecyl tetradecyl hexadecyl alcohol ethoxylate	68551-12-2
10	polyethylene glycol monolaurate	9004-81-3
	polyethylene glycol dilaurate	
	polyethylene glycol monoleate	
	polyethylene glycol dioleate	
	polyethylene glycol monotallate	
15	polyethylene glycol ditallate	
	sorbitan monolaurate	
	sorbitan trioleate	
	sorbitan monotallate	
	sorbitan trirallate	
20	polyethylene glycol glycerol cocate	
	caprylic triglyceride	
	polyoxyethylene tridecyl alcohol	24938-91-8
	polyoxyethylene lauryl ether	5274-68-0
	nonylphenoxypoly (ethyleneoxy) ethanol	9016-45-9
25	polyoxyethylene sorbitan monolaurate	
	sorbitan monolaurate polyoxyethylene polysorbate	9005-64-5
	polyoxyethylene oleyl alcohol	

30 The above list of suitable surfactants is not  
 exhaustive, but serves to illustrate twenty  
 representative examples of the many chemical  
 permutations possible with the family of polyol fatty  
 acid ester and ethoxylated ester type surfactants  
 useful for this invention.

35 The effectiveness of these surfactant  
 additives is readily apparent in their ability to  
 reduce the aqueous contact angle with cured or uncured  
 addition-curable polyvinylsiloxane dental impression

1 materials at temperatures in the range from 95°-110°C  
down to 30°C or less. Upon contact of the dental  
impression materials with the dentition and gingiva,  
any moisture present on the surface of these oral  
5 tissues is readily miscible with the surfactant moiety  
available at the surface of the impression material,  
which provides uniform wetting of the interface between  
the impression material and the oral tissues, thereby  
dramatically reducing surface tension.

10 The following Examples illustrate embodiments  
of the present invention. The concentrations are in  
weight percent unless otherwise stated.

EXAMPLE 1

Embodiments containing platinum black

15 for gaseous adsorption

BASE PASTE (VERY HEAVY VISCOSITY)

	<u>WT%</u>
vinyl polydimethylsiloxane	20%
hydropolydimethyl siloxane	3%
20 silicar filler	70%
liquid petroleum or other	
inert plasticizer	7%

CATALYST PASTE (VERY HEAVY VISCOSITY)

	<u>WT%</u>
25 vinyl polydimethylsiloxane	20%
*cyclic vinyl siloxane	0.4%
**chloroplatinic acid complex	1.0%
liquid petroleum or other	7%
inert plasticizer	7%
30 silica or other inert filler	71.6%

The following illustrates suitable  
compositional ranges for the components of the base and  
catalyst pastes.

	<u>WT%</u>
35 <u>BASE PASTE</u>	
vinyl polydimethylsiloxane	10-60
hydropolydimethyl siloxane	1-10
silica filler	20-80
liquid petroleum	0-15

1	<u>CATALYST PASTE</u>	<u>WT%</u>
	vinyl polydimethylsiloxane	10-60
	cyclic vinyl siloxane	0-2
	chloroplatinic acid complex	0.1-5.0
5	platinum black	0.2-20,000 ppm
	plasticizer	0-15
	filler	20-80

The following illustrates suitable  
compositional ranges for a cured dental impression  
10 material of the present invention.

	<u>VERY HEAVY VISCOSITY MATERIAL (PUTTY)</u>	<u>WT%</u>
	vinyl polydimethylsiloxane	10-60
	cyclic vinyl siloxane	0-1
15	hydropolydimethyl siloxane	0.5-5.0
	filler	20-80
	chloroplatinic acid complex	0.05-2.5
	platinum black	0.1-10,000 ppm
	plasticizer	0-15
20	surfactant	
	(optional but preferred)	2-10

\* Available under the tradename PSW 2204  
from Petrarch Silicones of Bristol, PA.

\*\* Available under the tradename PSW 2206  
25 from Petrarch Silicones of Bristol, PA.

Embodiments using surfactants to confer  
hydrophilic characteristics

EXAMPLE 2

	<u>Low viscosity catalyst paste with surfactant</u>	
30		<u>WT%</u>
	vinyl functional	
	polydimethylsiloxane	51.785
	siliceous filler	43.0
	n-dodecyl tetradecyl hexadecyl	
35	alcohol ethoxylate	4.0
	pigment	1.0
	cyclic vinyl functional	
	prepolymer	0.2



1	chloroplatinic acid catalyst	
	complex	0.01
	platinum black	0.005
		<hr/>
5		100.00
	Excellent hydrophilic surface characteristics, but unpleasant taste.	

EXAMPLE 3

	<u>Low viscosity base paste with surfactant</u>	
10	vinyl functional	
	polydimethylsiloxane	46.0
	siliceous filler	42.0
	hydrofunctional	
	polydimethylsiloxane	7.0
15	pigment	2.0
	nonylphenoxypoly	
	(ethyleneoxy) ethanol	3.0
		<hr/>
		100.0
20	Excellent hydrophilic surface characteristics and acceptable taste.	

EXAMPLE 4

	<u>Low viscosity base paste with surfactant</u>	
	vinyl functional	
25	polydimethylsiloxane	46.0
	siliceous filler	41.0
	hydrofunctional	
	polydimethylsiloxane	7.0
	n-dodecyl tetradecyl hexadecyl	
30	alcohol ethoxylate	4.0
	pigment	2.0
		<hr/>
		100.00

35      Excellent hydrophilic surface characteristics, but unpleasant taste.

Although the above examples are restricted to low viscosity polyvinylsiloxane dental impression materials, the same family of polyol fatty acid esters

1 and ethoxylated ester-type surfactants can be used as  
additives in the regular, heavy and even putty  
viscosities of the same type of material with equally  
effective results.

5 The following illustrates suitable  
compositional ranges for the components of the base and  
catalyst pastes of Examples 2 to 4.

	<u>BASE PASTES</u>	<u>WT%</u>
	vinyl polydimethylsiloxane	25-75
10	hydropolydimethyl siloxane	1-12
	siliceous filler(s)	25-75
	surfactant(s)	1-10
	pigment(s)	0.5
	<u>CATALYST PASTES</u>	<u>WT%</u>
15	<u>vinyl polydimethylsiloxane</u>	25-75
	cyclic vinyl siloxane	0.5
	siliceous filler(s)	25-75
	surfactant(s)	1-10
	pigment(s)	0.5
20	chloroplatinic acid complex	0.1-5.0
	platinum black	0.2-20,000 ppm

The following illustrates suitable compositional ranges  
for cured dental impression material(s) of Examples 2  
to 4 of the present invention:

	<u>LOW VISCOSITY MATERIAL (LIGHT BODY OR WASH)</u>	<u>WT%</u>
	Vinylpolydimethylsiloxane	25-75
	hydro polydimethylsiloxane	0.5-5.0
	cyclic vinyl siloxane	0-1
30	siliceous filler(s)	25-75
	surfactant(s)	1-10
	pigment(s)	0-5
	chloroplatinic acid complex	0.05-2.5
	platinum black	0.01-10,000 ppm

35 The following is a preferred embodiment of the  
present invention which exhibits the desired properties  
with respect to controlling outgassing and hydrophillic  
characteristics:

1	<u>LOW VISCOSITY BASE PASTE WITH SURFACTANT</u>	
		<u>WT%</u>
	vinyl functional	
	polydimethylsiloxane	
5	(4000 cps)	46.0
	calcium silicate filler	42.0
	hydrofunctional	
	polydimethylsiloxane	7.0
	nonylphenoxypoly (ethyleneoxy)	
10	ethanol	3.0
	cobalt blue pigment	2.0
		<hr/>
		100.00
	<u>LOW VISCOSITY CATALYST PASTE WITH PLATINUM</u>	
15	vinyl functional	
	polydimethylsiloxane	
	(4000 cps)	54.73
	calcium silicate filler	43.98
	cobalt blue pigment	1.0
20	cyclic vinyl functional	
	prepolymer	0.27
	chloroplatinic acid catalyst	
	complex	0.01
	platinum black (24 M <sup>2</sup> /gm)	0.01
25		<hr/>
		100.00

The following is a typical method used in preparing the compounds of the present invention. Other methods and compounds, such as those set forth in the above-mentioned US-A-4,273,902, may also be used in conjunction with this invention.

BASE PASTE

In a double planetary mixer, the three liquid components, viz. the vinyl functional polydimethylsiloxane, hydrofunctional polydimethylsiloxane and nonylphenoxypoly(ethyleneoxy) ethanol, are first blended together. The pigment is added and then the mixture is reblended to disperse the

1 pigment. The filler is then added and then the whole  
is mixed until thoroughly homogeneous, to form a  
low-viscosity fluid paste. The resulting paste is then  
rollmilled to maximize its homogeneity, followed by  
5 packaging as desired.

CATALYST PASTE

Preblends are made of (a) the chloroplatinic  
acid complex with a portion of the vinyl functional  
polydimethylsiloxane and (b) the platinum black with a  
10 portion of the calcium silicate filler. The three  
liquid components, viz. the catalyst complex preblend,  
the balance of the vinyl functional  
polydimethylsiloxane and the cyclic vinyl prepolymer,  
are then blended together. The pigment is then added  
15 and the mixture is reblended to disperse it. The  
platinum black preblend is then added, followed by the  
balance of the filler and mixing is continued until  
thoroughly homogeneous. Rollmilling to maximize  
homogeneity is then carried out, followed by packaging  
20 as desired.

While the invention has been described in  
detail with respect to specific embodiments thereof, it  
will be understood by those skilled in the art that  
variations and modifications may be made without  
25 departing from the essential features thereof.

30

35

1 CLAIMS:

1. A two-component dental impression material, which comprises a base paste and a catalyst paste, each containing a polyvinylsiloxane elastomer,  
 5 characterised in that the catalyst paste contains platinum black as a hydrogen gas adsorption agent.

2. A dental impression material according to claim 1, wherein the platinum black is present in an amount of up to 20,000 ppm by weight of the catalyst paste.

10 3. A dental impression material according to claim 1 or 2, which comprises:

	<u>BASE PASTE</u>	<u>WT%</u>
	vinyl polydimethylsiloxane	10-60
	hydropolydimethylsiloxane	1-10
15	silica filler	20-80
	liquid petroleum	0-15
	<u>CATALYST PASTE</u>	
	vinyl polydimethylsiloxane	10-60
	cyclic vinyl siloxane	0-2
20	chloroplatinic acid complex	0.1-5.0
	platinum black	0.2-20,000 ppm
	plasticizer	0-15
	filler	20-80

4. A dental impression material according to  
 25 claim 1, 2 or 3, wherein the platinum black has a size range of 18 to 28 Ångstroms.

5. A dental impression material according to any preceding claim, which contains a hydrophilic surfactant.

6. A dental impression material according to  
 30 claim 5, where the surfactant is selected from polyol fatty acid esters and ethoxylated esters.

7. A dental impression material according to claim 6, wherein the surfactant comprises at least one compound selected from:

35 n-dodecyl tetradecyl hexadecyl alcohol ethoxylate,  
 polyethylene glycol monolaurate,  
 polyethylene glycol dilaureate,  
 polyethylene monoleate,

1 polyethylene glycol dioleate,  
polyethylene glycol montollate,  
polyethylene glycol ditallate,  
sorbitan monolaurate,  
5 sorbitan monoleate,  
sorbitan trioleate,  
sorbitan monotallate,  
sorbitan tritallate,  
polyethylene glycol glycerol cocoeate,  
10 caprylic triglyceride,  
polyoxyethylene tridecyl alcohol,  
polyoxyethylene lauryl ether,  
nonylphenoxypoly-(ethyleneoxy)-ethanol,  
polyoxyethylene sorbitan monolaurate,  
15 sorbitan monolaurate polyoxyethylene polysorbate  
and  
polyoxyethylene oleyl alcohol.

8. A dental impression material according to any  
of claims 5 to 7, which comprises:

20	<u>BASE PASTE</u>	<u>WT%</u>
	vinyl polydimethylsiloxane	10-60
	hydropolydimethyl siloxane	1-10
	silica filler	20-80
	liquid petroleum	0-15
25	surfactant	1-10
	<u>CATALYST PASTE</u>	
	vinyl polydimethylsiloxane	10-60
	cyclic vinyl siloxane	0-2
	chloroplatinic acid complex	0.1-5.0
30	platinum black	0.2-20,000 ppm
	plasticizer	0.15
	filler	20-80

9. A cured dental impression, which comprises:

		<u>WT%</u>
35	vinyl polydimethylsiloxane	10-60
	cyclic vinyl siloxane	0-1
	hydropolydimethyl siloxane	0.5-5.0
	filler	20-80

1 chloroplatinic acid complex 0.05-2.5  
platinum black 0.1-10,000 ppm  
plasticizer 0-15

10. A dental impression according to claim 9,  
5 which also contains 1 to 10 WT% of at least one hydrophilic surfactant.

11. A polyvinylsiloxane catalyst paste, which comprises a polyvinylsiloxane elastomer, characterised in that up to 20,000 ppm of finely-divided  
10 platinum black is included, which functions to adsorb hydrogen gas generated on reaction of the catalyst paste with a hydrofunctional polydimethylsiloxane.

12. A catalyst paste according to claim 11, wherein the platinum black is present in a concentration in  
15 the range from 0.2 to 20,000 ppm by weight.

13. A catalyst paste according to claim 11 or 12, wherein the platinum black has a size range of 18 to 28 Angstroms.

14. A catalyst paste according to any of claims  
20 11 to 13, which has the following composition:

vinyl polydimethylsiloxane  
cyclic vinyl siloxane  
chloroplatinic acid complex  
platinum black  
25 plasticizer  
filler.

15. A catalyst paste according to any of claims 11 to 14, which contains a hydrophilic surfactant selected from polyol fatty acid esters and ethoxylated esters.

30 16. A catalyst paste according to claim 15, wherein the surfactant comprises at least one compound selected from:

n-dodecyl tetradecyl hexadecyl alcohol ethoxylate,  
polyethylene glycol monolaurate,  
35 polyethylene glycol dilaurate,  
polyethylene glycol monleate,  
polyethylene glycol dioleate,  
polyethylene glycol monotallate,

1 polyethylene glycol ditallate,  
sorbitan monolaurate,  
sorbitan monooleate,  
sorbitan trioleate,  
5 sorbitan montallate,  
sorbitan tritallate,  
polyethylene glycol glycerol cocate,  
caprylic triglyceride,  
polyoxyethylene tridecyl alcohol,  
10 polyoxyethylene lauryl ether,  
nonylphenoxypoly (ethyleneoxy) ethanol,  
polyoxyethylene sorbitan monolaurate,  
sorbitan monolaurate polyoxyethylene polysorbate  
and  
15 polyoxyethylene oleyl alcohol.

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# EUROPEAN SEARCH REPORT

00268347

Application Number

EP 87 30 4390

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 046 907 (BAYER) * Examples 2,3 * ---	1-4,8,9 ,11-14	A 61 K 6/10 C 08 L 83/04
Y	H. RÖMPP: "Chemie Lexikon", 5th edition, 1962, pages 3952-3953, Franckh'sche Verlagshandlung, Stuttgart, DE; * Page 3952: "Platin" * ---	1-4,8,9 ,11-14	
A	EP-A-0 117 056 (TORAY SILICONE CO.) * Page 7, paragraph 4; page 12, lines 10-11 * ---		
A	US-A-4 020 014 (A. SERVICE) * Column 4, lines 25-41 * -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			A 61 K C 08 K C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03-02-1988	Examiner COUSINS-VAN STEEN G.I.L.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	